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FIELD MUSEUM OF NATURAL HISTORY

Volume 16 DECEMBER 19, 1969 No. 15

Mineral Assemblages and the Chemical History of Chondritic Meteorites

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ABSTRACT

An attempt has been made to correlate the mineralogical and bulk chemical characteristics and the textural and structural features of chondritic meteorites.

The thermodynamic basis for the observed mineral assemblages of the ordinary chondrites is discussed in some detail with respect to the temperature of crystallization, state of oxidation and the liquidus relations. The approximate oxidation fields of the ordinary, enstatite and carbonaceous chondrites are delineated and compared with a gas of solar composition. It is shown that the field of the ordinary chondrites is quite well defined and that these chondrites are more oxidized than the solar gas so that direct condensation from this medium is excluded. The evidence for initial high temperature liquidus crystallization for most ordinary chondrites is discussed, and it is concluded that the chondrites of uniform composition probably represent rapid crystallization through liquidus temperatures, with perhaps some annealing to a near equilibrium distribution of Mg and Fe^{2+} just below the liquidus. The nonuniform, disequilibrium chondrites appear to represent, in part, a lower rate of cooling and crystallization and show evidence that they originated under conditions of varying oxidation.

The observed textural features of the metal grains of most ordinary chondrites with the coexisting silicates are interpreted as having resulted, not from any magmatic or mechanical processes but from transport and deposition from the vapor phase. This accounts well for nearly all the observed textural and structural features.

The analytical relations are derived relating the normative olivine contents of the chondrites to the ratio of oxidized to reduced iron and consequently to the degree of oxidation. This derived relation is then compared with that observed for 43 chondrites and a good correspondence is found. This again tends to support

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the approximate validity of Prior's rules when account is taken of analytical errors and a certain amount of variation in the bulk composition.

A critique is also presented of certain views on the origin of chondrites which depend primarily on mineral chemistry and little agreement with these is found.

INTRODUCTION

In the past many hypotheses have been advanced for the origin of various classes of meteorites with the chondrites receiving the most attention. Concentration in these studies has been largely on the bulk chemical properties, but recently a keener appreciation for the importance of mineral chemistry and phase equilibria has been apparent. It has been more widely recognized that the relations between coexisting mineral phases are detailed expressions of the environment of crystallization and that it is more informative to work with minerals and their inter-relations than with bulk meteorites.

Recent detailed studies of the chondrites have revealed that they may be divided into two types depending on whether or not the silicates of a given meteorite are of almost constant composition throughout the meteorite and whether or not magnesium and ferrous iron are distributed in an orderly way between the silicates. The critical questions involved here are the mode of crystallization that can account for the textural and chemical characteristics in each case, whether or not crystallization was from a melt, the rapidity of this crystallization and the extent to which equilibrium was attained. Since it has also been frequently proposed that some chondrites have undergone metamorphism or recrystallization, it is desirable to see to what extent this hypothesis is compatible with the observed textures and predicted chemical relations. One of the most critical sets of data in this study is that relating to the temperature coefficient of the distribution of Mg and Fe^{++} among the coexisting olivines and pyroxenes since it may tell us the temperature of crystallization and whether or not a given meteorite has been recrystallized. Unfortunately, the experimental and observational data bearing on this problem are as yet inconclusive because of the large experimental uncertainties (Mueller, 1964). However, in the past the high temperature experimental data have been almost completely ignored by the advocates of metamorphism. We believe that these data require consideration in any interpretation of the temperature of crystallization.

Another important issue concerns the disposition of the metal grains in chondrites, the mechanism by which these grains arrived at their present positions and their chemical relations to the silicates.

Then, also, the sequence of meteoritic types discovered by Prior (1916a) which presumably reflects different degrees of oxidation, implies a systematic and predictable variation in the norms of the minerals according to the reaction, pyroxene + metal + $O_2 \rightarrow$ olivine. It is interesting to compare these theoretical norms with those calculated from the analyses, since this provides a further test of Prior's rules.

In this paper an attempt is made to answer some of these questions or at least to set limits to which hypotheses must conform regardless of specific modes of origin. While no attempt is made to review[1] again all the hypotheses proposed previously, a critique of certain views which depend primarily on mineral chemistry is presented and these are compared with observational data and thermodynamic and kinetic considerations.

PHASE RELATIONS

Equilibrium Between Crystals and Gases

The major phase relations among the crystalline phases and with the associated gas may be expressed in terms of the following reactions (Mueller, 1963):

$$(1)\quad \underset{\text{olivine}}{\tfrac{1}{2}Mg_2SiO_4} + \underset{\text{pyroxene}}{FeSiO_3} \rightleftharpoons \underset{\text{olivine}}{\tfrac{1}{2}Fe_2SiO_4} + \underset{\text{pyroxene}}{MgSiO_3}$$

$$(2)\quad \underset{\text{pyroxene}}{2MgSiO_3} + \underset{\text{metal}}{2Fe} + \underset{\text{gas}}{O_2} \rightleftharpoons \underset{\text{olivine}}{Fe_2SiO_4} + \underset{\text{pyroxene}}{Mg_2SiO_4}$$

$$(3)\quad \underset{\text{pyroxene}}{FeSiO_3} + \underset{\text{metal}}{Fe} + \underset{\text{gas}}{\tfrac{1}{2}O_2} \rightleftharpoons \underset{\text{olivine}}{Fe_2SiO_4}$$

Only two of these reactions are independent, so that any two may be used in the analysis of the phase relations. However, because of the lack of reliable thermal data for $FeSiO_3$ (ferrosilite), it is convenient to use (1) and (2) rather than (3). Then the corresponding equations of equilibrium may be written as

$$(4)\quad K_1 = \frac{X_{Mg}^{px}\,(1 - X_{Mg}^{ol})}{X_{Mg}^{ol}\,(1 - X_{Mg}^{px})}$$

[1] A comprehensive review of the various hypotheses on the origin of the various meteorite classes, including the chondrites, has recently been presented by Anders (1964).

$$(5) \quad K_2 = \frac{(X^{ol}_{Mg})^2 \ (1 - X^{ol}_{Mg})^2}{(X^{px}_{Mg})^2 \ (a^{M}_{Fe})^2 \ P_{O_2}}$$

In these expressions X(ol/Mg) and X(px/Mg) represent the atomic fraction $Mg/(Mg+Fe^{2+})$ in olivine and pyroxene respectively; a (M/Fe), the relative activity of iron in the metal; and $P(O_2)$, the fugacity of oxygen. In the derivation of these equations, it has been assumed, on the basis of certain criteria (Mueller, 1964), that both olivines and pyroxenes behave essentially as ideal solutions.

If equation (4) holds approximately, then, as was shown by Ramberg and DeVore (1951), the coexisting olivines and pyroxenes provide us with a simple thermometer for the environment of crystallization. It was previously shown (Mueller, 1964), on the basis of optical data obtained by Ringwood (1961) that for the chondritic meteorites K_1 approximates 1.13, and it was argued that this coefficient decreases with increasing temperature.[1]

Recently, a valuable body of new data on the compositions of coexisting olivines and pyroxenes from 95 chondrites was presented by Keil and Fredriksson (1964). These data were obtained on the the electron microprobe and appear to be of a high order of precision. Of the total, 86 specimens showed almost constant or uniform composition of the silicates throughout the individual meteorite specimen. Keil and Fredriksson termed these "ordinary chondrites"; however, we shall refer to them as "uniform chondrites" since the term "ordinary" is usually applied to a broader class. The values of $Fe^{2+}/(Fe^{2+}+Mg)$ for the 86 uniform chondrites have been plotted on the conventional Roozeboom diagram in Figure 1. These data agree to a surprising degree with the optical data of Ringwood (1961) but show a more distinct division into three groups which coincide with high (H) and low (L) iron groups of Urey and Craig (1953) and a group designated "LL" by Keil and Fredriksson. This latter group has been included with the L group here.

The data representing the latest experimental work on this system are also shown in Figure 1. It may be significant that of the points representing intermediate values[2] of $Fe^{2+}/(Fe^{2+}+Mg)$, those

[1] The opposite result was obtained by Craig (1964). However, his conclusion is unwarranted when account is taken of uncertainties in the data used.

[2] It may be shown that values of K_1 calculated from extreme values of $Fe^{2+}/(Fe^{2+}+Mg)$ have greater uncertainties than those calculated from intermediate values.

of Ernst lie farthest from the 45° line. Since these represent the lowest temperatures of synthesis (~1200°K), they are consistent with a high temperature of crystallization for the chondrite mineral pairs.

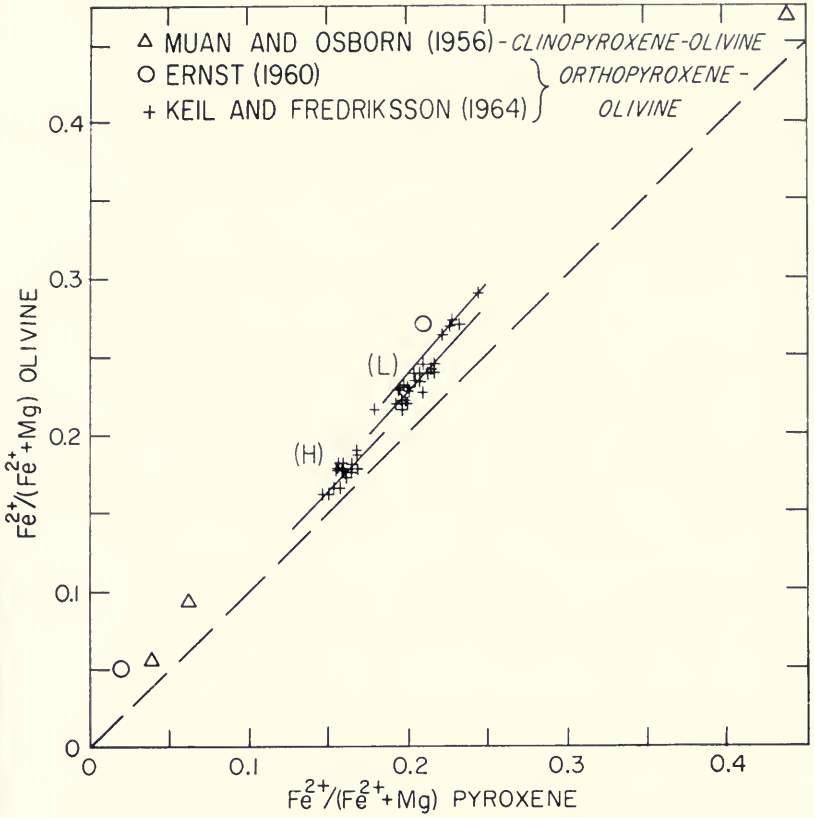

FIG. 1. Compositions in terms of atomic fractions of coexisting olivines and pyroxenes of 84 uniform chondrites as compared with experimental data. The lines which pass through the three groups of meteorite points approximate distribution curves based on ideal solutions. These data are compatible with a distribution constant which decreases with increasing temperature. Some points, which fell too close to others, were not plotted in this figure.

If we examine the distribution of points representing the chondrite minerals in Figure 1, we see that the three groups lie at successively greater distances from the 45° line, with the highest iron group closest to the line. Also, it is apparent that each distribution is somewhat linear and oriented approximately parallel to the curves representing the types of distributions defined by equation (4), although

it is patently impossible to tell from the data whether this relation is obeyed over greater ranges of composition. Three such curves have been drawn to pass through the three groups. Thus, if, as we have indicated, K_1 decreases with increasing temperature, then the high iron group represents the highest temperature of crystallization. We shall see that there is consistency between this result and the expected partitioning under conditions of rapid crystallization at liquidus temperatures.

The link between the solid solutions and the associated gases is provided by equations (4) and (5) solved to eliminate either X(ol/Mg) or X(px/Mg). It is convenient to discuss the equations first in terms of the pure system Fe-MgO-SiO_2-O_2 with a (M/Fe)=1. We may then evaluate the effect of variable nickel content of the metal phase separately. Under these circumstances $P(O_2)$ is a univariant function of the temperature if one of the parameters X(ol/Mg) or X(px/Mg) is arbitrarily fixed.[1] The results of such calculations for three silicate compositions are plotted in Figure 2 where they have been superimposed on the stability fields of the pure iron oxides. However, the field of wüstite has been omitted since it does not appear as a phase in these high silica systems.

In Figure 2 we have roughly delimited the fields of the various types of chondritic meteorites as they appear from observational data and theoretical considerations. We have also drawn a curve in Figure 2 that represents the degree of oxidation, over the entire temperature range, of a gas of solar composition as given for the solar abundances tabulated by Aller (1961). This calculation is based on the reaction

$$(6) \quad \overset{\text{gas}}{H_2} + \overset{\text{gas}}{\tfrac{1}{2}O_2} \rightleftharpoons \overset{\text{gas}}{H_2O}$$

The equation of equilibrium for this reaction may be written as follows according to the method of Urey (1952):

$$(7) \quad \log P_{O_2} = 2 \log (2 A_O / A_H) - 2 \log K_6$$

Here A(O) and A(H) are the total relative solar abundances of oxygen and hydrogen respectively. Over most of the temperature range of interest, the oxygen will be tied up predominantly in H_2O and CO

[1] We assume here that the total gas pressure is small enough to have negligible effect on the solids.

since CO_2 becomes an important species only below 400°K[1] and no other element is abundant enough to preempt much oxygen. This may be seen as follows: If we arbitrarily set $A(H)=10^{12}$, then $A(O)=10^{8.96}$ and A(C), the abundance of total carbon, is $10^{8.72}$. The next most abundant constituents Si and Mg have abundances of only $10^{7.50}$ and $10^{7.40}$ respectively.

For the higher hydrogen pressures methane is the only important carbon species but at lower pressures CO dominates. For example, at 800°K $P(CO=P(CH_4)$ at $P(H_2) \sim 10^{-2}$ atm. In calculating the curve of Figure 2, it was assumed that the total pressure was high enough to keep all the carbon as methane. However, if we had assumed that all the carbon occurred as CO (corresponding to low pressures), the equation (7) would be rewritten as

$$(8) \quad \log P_{O_2} = 2 \log (0.85 A_O / A_H) - 2 (\log K_6)$$

It is apparent that on the scale of Figure 2, this shifts the curve only slightly.

The field of the ordinary chondrites is fairly well defined in Figure 2. In terms of $\log P(O_2)$, it is limited approximately by the values corresponding to 0.22 and 10^2 for X(ol/Mg), since ordinary chondrites have silicates only slightly more iron rich than this and none is more magnesium rich. We have already indicated that K_1, as determined from Figure 1 is consistent with high temperatures of crystallization. Miyashiro (1962a) also found that those meteorites commonly contain high temperature plagioclase. Further evidence that most of these meteorites represent crystallization at or near liquidus temperatures will be discussed later. Thus, it is natural that we choose these liquidus temperatures of approximately 1800°K as defining the upper temperature limit of the field. However, the lower temperature limit is more difficult to fix and we have somewhat arbitrarily set it at 1000°K.

It has already been shown (Mueller, 1964) that some of the most common gases in equilibrium with material of chondritic composition are H_2 and CO rather than H_2O and CO_2, which are so important in geologic processes. Thus, the behavior of systems such as melts, which absorb these gases, may be quite different from their terrestrial counterparts. Also, we must remember that the equilibrium complement of gases is unlikely to be retained by the meteorites without contamination or alteration so that it is not generally safe to draw

[1] This and other conclusions regarding the solar gas are based on unpublished calculations by one of us (Mueller, MS).

conclusions from gas analyses without determining their compatibility with the state of oxidation of the meteorite.[1]

Although the ordinary chondrites are quite reduced by terrestrial standards, they are far less so than the enstatite chondrites. It is obvious from the mineralogy of the latter meteorites (Mason, 1962) that their field of crystallization lies at considerably lower values of P_{O_2} than ordinary chondrites (Olsen and Fuchs, 1967). This is shown, for example, by the analysis of such reactions as the following

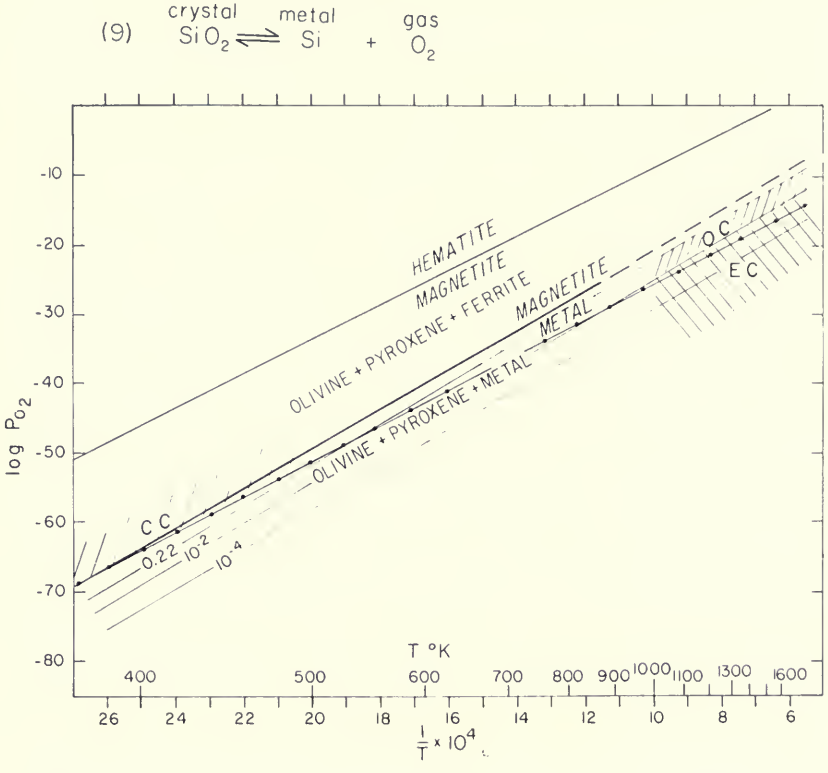

FIG. 2. Approximate fields, in terms of oxidation, of the three major chondrite groups. The following fields are designated: OC=ordinary chondrites, EC=enstatite chondrites and CC=carbonaceous chondrites. The light numbered curves indicate olivine compositions for the assemblage olivine-pyroxene-metal-gas. The dot-dash curve indicates a gas of solar composition with hydrogen pressures adequate to maintain most carbon as methane. Of the three groups, only the field of the ordinary chondrites is well defined.

[1] We should suspect gas analyses which contain high CO_2/CO ratios such as the New Concord chondrite analyzed by Wright (1876) and quoted by Mason and Wiik (1961). It seems virtually certain that the high CO_2 values result from either late oxidation, adsorption of CO_2 or simply from analytical errors.

Preliminary results (McCallum, 1965) indicate that log $P(O)_2$ curve for (9) lies near the center of the area indicated for the enstatite chondrites in Figure 2 when account is taken of the silicon dissolved in the metallic phase.

The limits of crystallization of the carbonaceous chondrites are particularly ill defined. Many of these meteorites contain two fractions which appear to have been formed under greatly different conditions (Dufresne and Anders, 1962). The matrix, which tends to dominate, frequently consists of an intimate mixture of carbonaceous materials such as complex hydrocarbons, magnetite and serpentine-like silicates, whereas the chondrules consist of olivine and pyroxene which appear to have crystallized under higher temperatures and more reducing conditions. This is especially marked in the Murray carbonaceous chondrite in which some olivine chondrules include spheres of nickel-iron that appear to have been molten (Fredriksson and Keil, 1964).

The hatched area by which we designate the field of the carbonaceous chondrites in Figure 2 thus applies largely to the matrix material. Although most of this area falls in the field of magnetite, it also is astride the magnetite-metal boundary to take into account the presence of some metal. It is interesting that the oxidation curve for the solar gas crosses into the magnetite field in this region close to 400°K, and it may be that this has some significance in the history of these chondrites.

Liquidus Relations Among the Silicates

The crystallization history of the ordinary chondrites can be understood only in terms of the liquidus relations in the subsystem MgO-FeO-SiO_2 or in the somewhat more complex system of the meteorites themselves. The major features of the subsystem were worked out by Bowen and Schairer (1935).[1] Their results are shown in Figure 3 in terms of the mole fractions of the components. This method of plotting is preferred over the more familiar weight-percent plot since it exhibits the inherent symmetry of the system and is at the same time directly comparable with other molar plots, such as Figure 1.

In Figure 3 we have plotted the mean tie lines and normalized mean bulk composition points for the high and low iron groups.

[1] Actually Bowen and Schairer worked in the system Fe-MgO-SiO_2-O_2. However, the extra component is compensated by the extra phase represented by the iron crucibles in which the experiments were conducted.

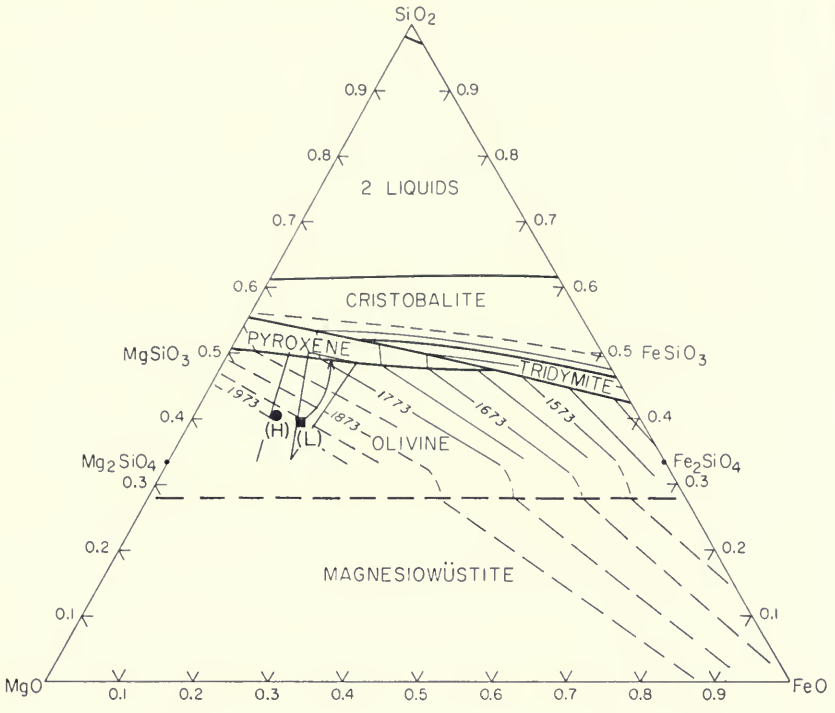

FIG. 3. Liquidus relations in the system MgO-FeO-SiO_2 after Bowen and Schairer (1935). The diagram is plotted in terms of mole fractions of the components. The two points in the olivine field refer to the arithmetic means of the bulk compositions of 16 low (L) and 16 high (H) iron chondrites whose minerals were also analyzed by Keil and Fredriksson (1964) (see Table 1). The two mineral tie lines shown refer to arithmetic means of the corresponding coexisting mineral compositions. A liquid-crystal tie line for the low iron group is also shown. In addition, a curved path of equilibrium crystallization is shown diagrammatically.

The data on which these values are based are given in Table 1. The normalized points for the bulk compositions refer to mole fractions of MgO, FeO and SiO_2 after the subtraction of quantities of these oxides corresponding to normative feldspars, wollastonite, etc.

We have also drawn as an illustration in Figure 3, the approximate tie line, as determined by Bowen and Schairer, between the silicate minerals of the low (L) iron group and the equilibrated liquid. The composition so defined represents the last small quantity of liquid in equilibrium with the crystals at the end of the path of equilibrium crystallization in the field of olivine.

If the bulk chemical analyses agreed perfectly with the mineral compositions as determined from the electron probe analyses, the

points would fall directly on the corresponding tie lines. Although these points are not far off, they are sufficiently off to show that errors are involved. The direction of displacement of the points indicates that too much FeO appears in the bulk analysis. This would be expected if oxidation of some metal had occurred or if metal were present as inclusions within the silicates. Since both of these sources of error should occur quite frequently, this deviation is understandable.

In the use of Figure 3, it is important to keep in mind what occurs during the course of various types of crystallization. For bulk compositions like the chondrites, the first crystal to separate is a Mg-rich olivine if there is sufficient time for this to occur. The composition of the liquid then follows the curved path to the phase boundary with pyroxene, and both minerals crystallize simultaneously. The composition of the liquid moves along the boundary, and if equilibrium is maintained by constant adjustment of crystal[1] composition to liquid, crystallization ends when the olivine-pyroxene tie line intersects the bulk composition point.

If, on the other hand, Mg-rich crystals are continuously withdrawn by some such mechanism as crystal settling in a gravitational field or armoring, then the composition of the liquid may move farther along the pyroxene-olivine boundary. Such fractional crystallization is equivalent to changing the bulk composition and thus moving the total composition point. This may also be accomplished by changing the oxidation state during crystallization. For example, if $P(O)_2$ is arbitrarily decreased, the bulk composition point will move directly away from the FeO corner toward the $MgSiO_3$-Mg_2SiO_4 join. It should be observed that such movement is nearly parallel to the isotherms of Figure 3 and thus does not involve much of an increase in liquidus temperatures. We shall see that such a mechanism of changing $P(O)_2$ is capable of explaining certain peculiar compositional relations in some chondrites.

Because the bulk compositional points in Figure 3 represent the average high and low iron groups after the deduction of certain normative minerals such as the feldspars, these compositions cannot be directly related to the plotted isotherms of the subsystem MgO-FeO-SiO_2. The temperatures of the more complex liquidus of meteorites

[1] This seldom occurs in statically crystallizing silicate melts because activation energies are too high to permit the required exchange diffusion from the interior of the crystal. Thus, equilibrium crystallization of this type is only a formal idealization.

may lie roughly 100°K lower.[1] Thus, crystallization of the high (H) iron group should begin at about 1850°K whereas that of the low (L) group should begin at about 1825°K.

The relations just discussed show that there is no simple connection between the composition of coexisting chondritic olivines and pyroxenes and any hypothetical liquid which has not reached the olivine-pyroxene boundary in equilibrium crystallization. This point was misinterpreted by Keil and Fredriksson (1964) who sought to relate the observed condritic olivine compositions to the composition of liquids in the olivine field as determined by Bowen and Schairer (1935). Their conclusion that more metal was oxidized at the time of crystallization than is observed at present is not demonstrable by such argument. In fact, the relation between the tie lines and the bulk composition points is not a matter of phase equilibria at all but is merely a condition of stoichiometry.

If an equilibrium path of crystallization had been followed, the final equilibration between crystals and liquid would have occurred at a lower temperature for the low (L) group than for the high (H) group with a difference of perhaps 25–50°K, if we assume that such substances as the feldspars lower the liquidus uniformly. Thus, there is a qualitative agreement between the different values of K_1 deduced from Figure 1 and the expected relation under equilibrium crystallization. However, we shall see that it is unlikely that crystallization occurred in this manner.

In addition to the equilibrium and fractional modes of crystallization, which occur under conditions of relatively slow cooling, it is necessary to consider a possible mechanism under conditions of rapid cooling. The evidence for rapid cooling of the silicates which comprise most of the chondrule types is of different kinds and has been discussed by numerous authors. This evidence takes the form of such features as microlitic, skeletal and radiating crystals combined with material that has the appearance of devitrified glass. The latter material sometimes shows typical glass fracture patterns. If crystallization-cooling is rapid enough, the rate of crystallization and the composition of the crystals and associated supercooled liquids or glasses will be restricted by the rate of diffusion. Thus, we can con-

[1] Alexeyeva (1958) describes melting experiments on whole meteorites in which melting began at 1453°K and was complete at 1623°K. Unfortunately, such data cannot be applied to the determination of liquidus temperatures for the *silicate component* of chondrites since oxidation of the metal, and the ferrous component in the silicates, interferes with this. Also, there is no evidence that the minimum requirement of a controlled atmosphere was used in the experiments.

ceive of a theoretical limiting case in which little or no change in the ratio of Mg Fe^{++} occurs on crystallization or congealing of the melt. However, it is unlikely that this case can be realized if any crystallization occurs since the time scales of crystallization and the distribution of Mg and Fe^{++} should both be governed by the time scale of diffusion. Thus, wherever olivine crystallizes there must be an outward diffusion of Si^{+} and an inward diffusion of Mg^{++} and Fe^{++}, and, therefore, a distribution of Mg^{++} and Fe^{++} consonant with an approach to equilibrium should also occur.

If, however, we assume the ideal limiting case, this may be illustrated as in Figure 4, which is a magnified part of Figure 3. If no distribution of Fe^{++} and Mg^{++} occurred on quenching of the chondrules, then all possible proportions of olivine and pyroxene lie on the dashed line ol′ – px″, which extends between the olivine and pyroxene joins and passes through the meteorite bulk composition point P. If any adjustment toward equilibrium, such as crystallization or recrystallization, followed the quenching process, then the limiting tie lines representing chondrules poor in pyroxene and chondrules poor in olivine would be ol′ – px′ and ol″ – px″, respectively while chondrules of unchanged composition would yield the tie line ol° – px°.

Vaporization of Metal

At the high temperatures of the silicate liquidus, and, in fact, down to temperatures of 1500°K, the vapor pressure of iron and nickel is appreciable. Consequently, transport and deposition of metals through the vapor phase could play an important role in the distribution of these substances in the chondrites. At 1700°K, the vapor pressure of iron is $10^{-4.86}$ atm., while at 1500°K it is $10^{-6.41}$ atm (Kubaschewski and Evans, 1958). The vapor pressure of nickel is similar but somewhat less. For example, at 1500°K it is $10^{-6.63}$ atm. There will be a mutual lowering of these pressures in the metallic solid and liquid solutions, but this should be so small that it is probably less than the errors involved in the thermochemical data for the vapor pressures of the pure substances.

RELATIONS BETWEEN THE NORMATIVE PHASE CONTENT AND THE BULK COMPOSITIONS

As originally stated, Prior's rules (Prior, 1916a) recognize the qualitative relations that exist between the silicate and metal com-

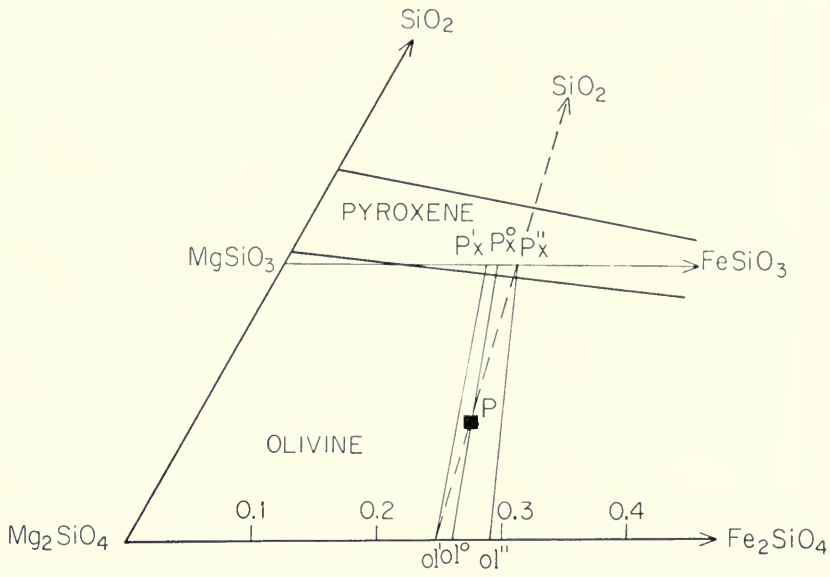

FIG. 4. Enlarged portion of Figure 3 to illustrate the idealized limiting case of rapid cooling and crystallization. The point P represents the initial bulk composition. The dashed lines ol'-P-Px'', which also passes through the SiO_2 apex, represents cooled mixtures of crystals or glass of varying olivine/pyroxene ratios and constant Mg/Fe^{2+}. The lines ol'-px', ol° px° and ol''-px'' represent near-equilibrium tie lines at temperatures which are probably just below the liquidus.

positions and between the quantities of reduced and oxidized iron.[1] The first quantitative expression of Prior's rules as concerns the amount of oxidized and reduced iron was provided by Urey and Craig (1953) who showed that the relation between these quantities must be linear with a negative slope if the rules are strictly applicable. The actual relation found by them from the meteorite analyses was only a crude approximation to that expression and showed clustering of the analyses into the familiar high and low iron groups.

The other part of Prior's rules, that relating the intensive compositional parameters of the silicates and metal was first discovered empirically by Ringwood (1961), but it was later shown (Mueller, 1963) that the observational curve agreed in form with that of the equation of condition for the oxidation of iron at constant Mg, Si,

[1] Prior believed that the sequence of types could be traced back to a parent magma of varying oxidation state. However, his observations do not require such a magma since all the relations could be derived equally by subsolidus oxidation or reduction.

Ni and total iron. The form of the curve generated is highly distinctive, and although Prior's rules may be satisfied in a variety of ways in a qualitative sense, only one general shape of curve is possible under the quantitative constraints.

Prior's oxidation sequence may be formally regarded as having originated by the displacement to the right of reactions (2) and (3).[1] If we begin with a meteorite of a certain fixed quantity of Mg, Si, Ni and total Fe, then the quantity of olivine increases from some initial value as pyroxene and metal disappear. Also, according to equation (5), $P(O)_2$ is approximately proportional to $X(ol/Fe)/a(M/Fe)^2$ if $X(ol/Fe) \sim X(px/Fe)$ is as shown by Figure 1. Thus, $X(ol/Fe) \sim X(px/Fe) \sim X(S/Fe)$, where X(S/Fe) refers to the silicates as a whole. Also, a(M/Fe) is approximately proportional to X(M/Fe)= Fe/(Fe+Ni) in the metal. The ratio X(S/Fe)/X(M/Fe), which we designate as R, is then a measure, in terms of intensive parameters, of the degree of oxidation. Thus, the olivine content is some increasing function of R. If we designate the molecular normative olivine content as L, we have the following definitions:

$$R = \frac{X^S_{Fe}}{X^M_{Fe}}$$

$$L = \frac{\text{moles } (Mg,Fe)_2SiO_4}{\text{moles } (Mg,Fe)_2SiO_4 + \text{moles } (Mg,Fe)SiO_3 + \text{moles metallic Fe}}$$

The analytical relation between L and R may be found by combining reactions (2) and (3) since the olivine content will depend only on the ratio (Mg, Fe)O/SiO_2 but not on MgO/FeO. Thus, we write

$$(10) \quad (Mg,Fe)SiO_3 + Fe + \tfrac{1}{2}O_2 \longrightarrow (Mg,Fe)_2SiO_4$$

At any stage of oxidation we designate the "extent of the reaction" in moles of reacted pyroxene and iron as α. Thus, each reacted mole of (Mg, Fe)SiO_3 and Fe produces one mole of (Mg, Fe)$_2SiO_4$. We designate the number of moles of pyroxene and metallic iron initially present as px° and Fe°, respectively. Also, if there is any olivine present at the beginning of the process we designate this as ol°. Since initially all the iron is reduced, ol° refers to Mg_2SiO_4 only.

[1] This formalism does not imply that the members of the sequence were necessarily derived from each other by either oxidation or reduction.

Thus, for any stage

$$(11) \quad R = \frac{\alpha[(Fe^{\circ}-\alpha)+Ni]}{(Fe^{\circ}-\alpha)(Px^{\circ}+2\,ol^{\circ}+\alpha)}$$

$$(12) \quad L = \frac{\alpha+ol^{\circ}}{px^{\circ}+ol^{\circ}+Fe^{\circ}-\alpha}$$

It is now possible to compare the theoretical relation between L and R with observed values of these quantities.

Observed values of L and R for 43 chondrites of uniform composition are given in Table 1 and are plotted in Figure 5. Most of these chondrites represent bulk analyses selected by Urey and Craig (1953) as "superior" and whose coexisting olivines and pyroxenes were analyzed by Keil and Fredriksson (1964). To this group have also been added certain specimens for which recent bulk analyses and mineral determinations were available and which served to extend the compositional range. In addition, one enstatite chondrite analysis, that of Daniels Kuil (Prior, 1916b), is also presented for comparison.

The arithmetic means of the various quantities of the high and low iron groups are also given in Table 1. The points representing these mean values are also shown in Figures 3 and 5. In Figure 5 a straight line was extended through these values for comparison with the distribution. It is apparent that this line must fall near any straight line approximation curve for the distribution, except that the latter would lie a little to the left of the plotted line. Nonetheless, the slope would be nearly the same. However, any such approximacurve would be meaningless since in theory the curve is not a straight line and, as we shall see, could not in any event accommodate the inhomogeneous data of Table 1.

In Figure 6 are shown examples of the family of theoretical curves obtained by the elimination of α from equations (11) and (12) and with the parameters Px°, Fe° and ol° in the range of meteorite compositions. We have also included the line of mean values from Figure 5, for comparison. Curve 1 of Figure 6 represents the hypothetical "pure enstatite chondrite" with ol°=0 and all initial Mg and Si occurring in pyroxene. Curves (2) and (3) represent more realistic compositions with initial olivine, which is equivalent to $MgOSiO_2$. These excess olivine contents may be compared directly with the mean values for the high and low iron groups of Figure 3 by projecting through their points from the FeO corner to the Mg_2SiO_4-$MgSiO_3$ join. Such a projection shows that L°, the initial value of

L, is approximately 0.1 for both groups but that it is a little smaller for the low iron group.

Although there is much scatter in the points of Figure 5, the distribution is obviously an approximation to the theoretical curves in the middle and upper ranges of values where the slopes are in essential agreement. The marked deviation in the lower range indicates that the bulk compositions are not constant and that crossing of the theoretical curves results. It has not been determined whether this is due to errors in the analyses or whether it results from the excess total iron content of the high iron group relative to the low iron group.

Figure 6 is an alternative quantitative expression of Prior's rules to the relations discussed earlier. The limits imposed on the observational evidence for Prior's rules have been discussed by a number of authors. For example, Craig (1964) is of the opinion that the chondrites as a whole approximate Prior's rules, but that the individual groups do not. However, it is difficult to see how this can be true since there are only two major groups and these groups are well distiguished by only certain types of data. For example, they are not well distinguished in Figure 5 which shows a continuous distribution of points. Keil and Fredriksson (1964) also attempted to show that the part of the rules relating to the quantities of oxidized and reduced iron did not hold. However, they plotted values for olivine and pyroxene separately (Keil and Fredriksson, 1964, fig. 11) without taking account of the total quantity of FeO as governed also by the amounts of these phases. This type of plot certainly cannot provide a test for the rules. Still, as was pointed out by these same authors, there are some large discrepancies between the ratio $Fe^{2+}/Fe^{2+}+Mg$) as calculated from the bulk compositions and the same quantity as limited by the observed mineral compositions. Some of these discrepancies show up clearly in Figure 5. For example, the two points representing Collespicoli and Djati-Pengilon, which lie farthest from the line in the lower part of the diagram, show very large discrepancies of this type (Keil and Fredricksson, 1964, table 6). Yet some other specimens such as Tomhannock Creek and Forksville, which also show discrepancies, do not plot unusually far from the line. In such cases the scatter attributable to analytical error is probably compensated by some other factor. This is quite possible since, even if all chemical analytical errors were absent, great scatter could still occur because of the expected independent variations in MgO, SiO_2 and total Fe, which to a large extent are also responsible for deviations from Prior's rules.

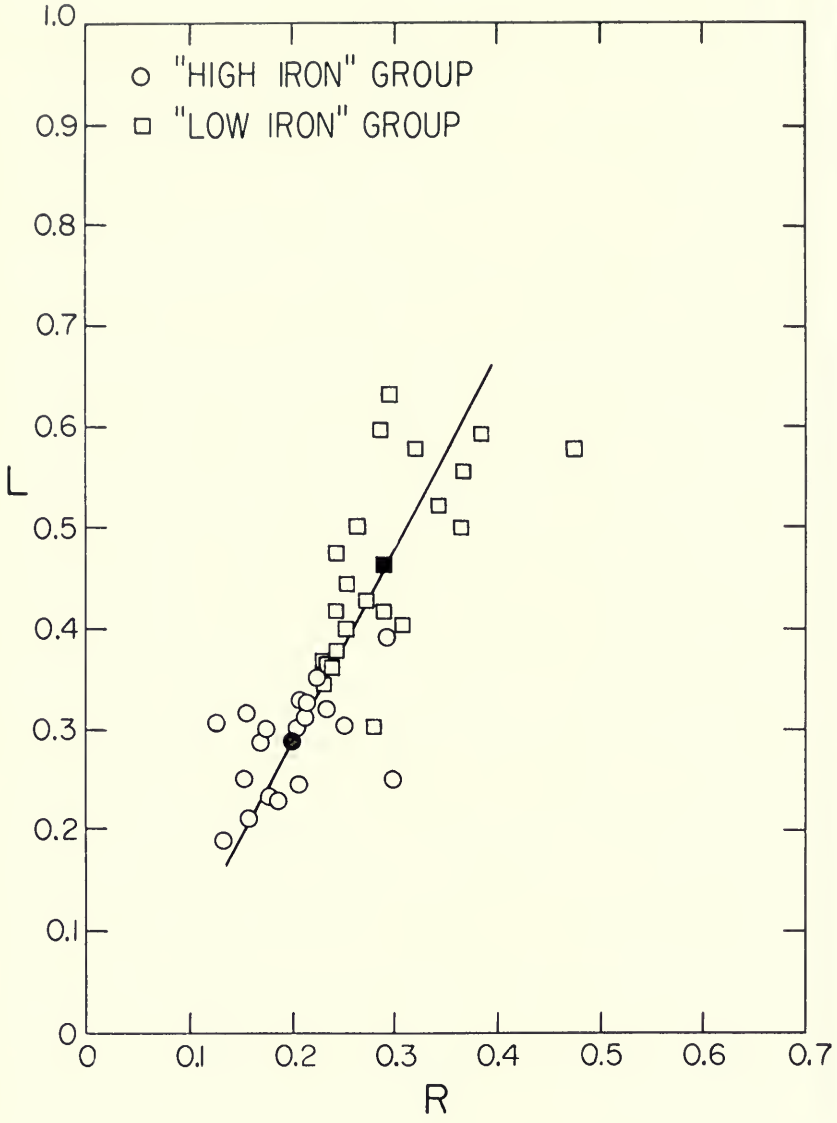

FIG. 5. Molecular normative olivine content L, of 43 uniform chondrites plotted against the ratio of oxidized to reduced iron R (see text). The straight line joins the arithmetic means of the high and low iron groups.

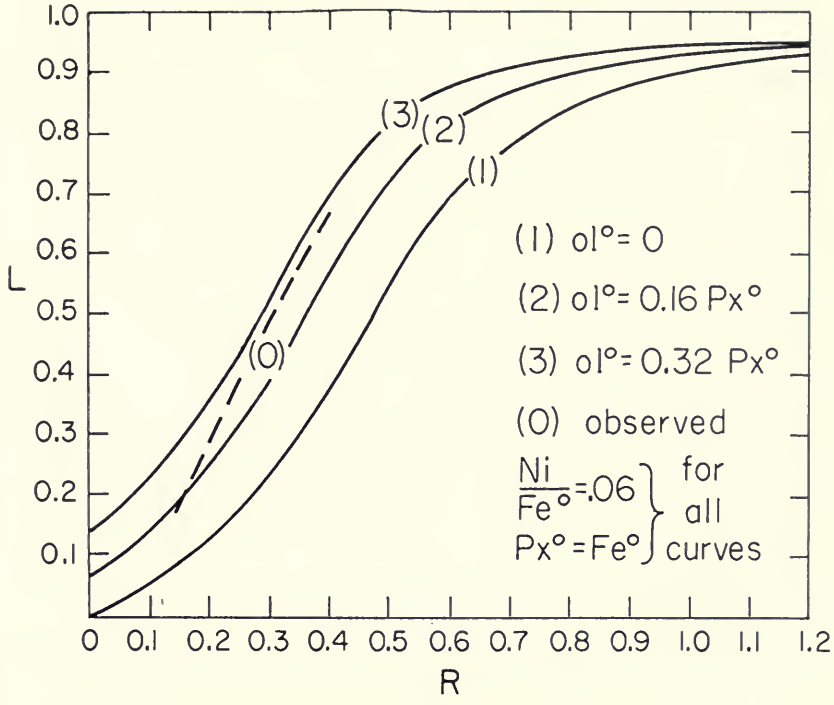

FIG. 6. Theoretical plot of the molecular normative olivine content L as a function of R for various Mg/Fe^{2+} ratios expressed or "initial olivine" ol°. The line (0) of mean values is the same as that shown in Figure 5. Note the similarity of slopes of (0) and curve (3) in the upper and middle ranges and the divergence of the two slopes in the lower range of (0).

RELATIONS BETWEEN MINERAL CHEMISTRY AND TEXTURES

CHONDRITES OF UNIFORM COMPOSITION

Comprehensive knowledge of the history of the chondritic meteorites can come only through the interpretation of their textures and the correlation of grain and chondrule types with the mineral chemistry. This is more difficult than the deduction of the physicochemical environment from phase relations since we are here faced with identifying the mechanisms which comprise what may have been a complex series of interwoven chemical and mechanical events. Given this state of affairs, it seems desirable to copy to a certain degree our procedure in phase equilibrium studies and discuss only

those mechanisms of sufficient generality to encompass the most observations.

The division of the chondrites into a uniform or "equilibrium" type, on one hand, and variable or nonequilibrium type, on the other, is convenient, but it is probable that a gradation between the two groups exists. The nature and orderliness of the distributions of Mg and Fe^{2+} shown by Figure 1 points to the attainment of a measure of chemical equilibrium; however, it seems improbable that perfect equilibrium was ever attained even within this group. This may be seen by considering the mixture of phases of different densities which comprise these bodies. If even a weak gravitational field existed at the place of formation, it is certain that the bodies were not in mechanical equilibrium (and hence also not in perfect chemical equilibrium), since there should then have been a segregation of silicate and metal phases. Of course, this state of mechanical disequilibrium is common enough in terrestrial metamorphic rocks which exhibit a fairly close approach to local chemical equilibrium.[1] The explanation is to be found in the high viscosities of solids which prevent their attaining the level appropriate to their densities. However, if the metal and silicate components of meteorites had been associated when either or both were molten, separation should have occurred in a gravitational field.

Any cursory examination of large slabs of chondrites (such as those in the Field Museum of Natural History) reveals their striking uniformity in the distribution of metal grains. However, many of these same specimens, some of which range up to 0.5 meter in dimension, also contain segregations of metal in the forms of veins which appear to mark healed fractures. Specific examples of such meteorites are the chondrites Farmington, Cullison, Bluff, Arapahoe and Rose City. Also, it is well known that the metal grains are usually highly irregular and of an interstitial character. A typical relation between the metal and silicates is shown in Figure 7 from the chondrite Allegan. The metal here is closely molded to the chondrules but is not restricted to any one chondrule. Metal apophyses extend into the surrounding matrix of silicates.

These facts regarding the form and disposition of metal grains within the body of the meteorite and the segregation into veins seem to argue for a high degree of mobility of the metal after or at the time of consolidation of the bodies. They thus appear to rule out both

[1] This local equilibrium is usually restricted to volumes less than one cubic centimeter (Mueller, 1960).

FIG. 7. Drawing of thin section of the chondrite Allegan illustrating typical silicate-metal relations.

magmatic and mechanical processes as important in the formation of the existing textural relations.

A detailed study of the structural and textural relations of metal particles in chondrites was undertaken by Urey and Mayeda (1959). Many of the grains observed by them seemed to exhibit complicated mechanical and thermal histories. Some grains were found to consist of plessite while others combined large crystals of pure kamacite and taenite. In a few cases truncated diffusion borders indicated mechanical disruption. From this Urey and Mayeda concluded that the grains had been derived from a pre-existing "primary object" which had been broken up and reconstituted to form the meteorites.

However, R. E. Marringer (Mason and Wiik, 1961) has discussed this problem in terms of the Mocs chondrite and concluded that the disruption of metal grains appears to have occurred essentially in place. As we shall see, it is also easy to account for such features as individual crystals of kamacite and taenite which were not derived by unmixing.

One of the best known mechanisms of crystallization and mineral-forming processes is deposition from a fluid or vapor phase. We have already called attention to the high vapor pressures of the metals near the silicate liquidus and indicated that this favored rapid transport and deposition of metal. There is also experimental evidence which supports this contention. Thus, Morelock (1962) described the growth of iron whiskers from vapor at temperatures as low as 1333°K with 200μ whiskers formed in 16 hours.

The deposition of iron and nickel from the vapor phase goes a long way in explaining the observed textural features. It accounts especially well for the interstitial and irregular character of the metal particles, and the common occurrence of veins indicates that transport and deposition continued after the meteorites consolidated enough to fracture. This type of deposition is also capable of accounting for the variety of occurrences of kamacite and taenite observed by Urey and Mayeda (1959). Thus, for example, isolated grains of either of these might grow from the vapor below the transformation curve without the appearance of exsolution textures. However, such low temperature growth should be much slower than that just below the silicate liquidus.

If growth occurred from the vapor phase, one might expect some relation between the distribution of metal grains and the available interstitial space. It seems conceivable that the excess iron of the high iron group might therefore be attributable to a higher porosity at the time of consolidation. If consolidation of the chondrites occurred in some type of parent body with a metal core, it might have happened that iron vapor transported from the hot, metal-rich interior deposited between the silicate grains, filling most of the available space.

There can be very little doubt that the unique textural features of the chondrites result from some mode of crystallization on the liquidus. This crystallization mechanism has time after time given rise to a variety of chondrule forms which fall roughly into the following major groups: 1) barred olivine with interstitial rest crystals or glass, 2) porphyritic olivine with a microcrystalline ground mass

or glass, 3) granular olivine with a microcrystalline ground mass or glass and 4) nearly pure pyroxene chondrules, usually with an eccentric radiating structure. Frequently all four forms of these chondrules occur within the same thin section although they may vary greatly in abundance. Furthermore, they seem to occur without any obvious relation to the ordinary chondrite subdivisions. They are all common in both the high and low iron groups and within the uniform and variable chondrites as well. For example, such high iron group uniform chondrites as Allegan, Barbotan and Kesen all contain a variety of well-defined chondrules as do also the low iron group representatives Albareto, Alfinanello, Aussun and Bjurböle.[1] In most of these chondrites the glassy-appearing material has apparently devitrified or consisted of microcrystals from the start. However, fairly convincing evidence for true glass in the Breitscheid chondrite was presented by Hentschel (1959). Yet recently much emphasis has been given by Wood (1963a) to a few low-iron group chondrites, such as Lissa and Bath Furnace, that show only a few well-developed chondrules, and these have been taken to represent the end products of a metamorphic sequence.

In the uniform chondrites we are then faced with the difficulty of reconciling the coexistence in a single meteorite of widely different chondrule types with the apparent uniformity of mineral composition throughout the specimen and with the additional evidence of rapid quenching from the liquidus. Thus, if we accept the results of the electron probe, optical and X-ray investigations, this uniformity applies to chondrules of nearly pure olivine and to those of nearly pure pyroxene. If we assume that each chondrule represents a specimen of pure liquid or of a liquid-crystal suspension, then systems of varying composition always gave rise to the same mineral compositions. This was refered to as "Fredriksson's paradox" by Suess (1964) and is an impossible state of affairs under either equilibrium or fractional crystallization.

Keil and Fredriksson (1964) found it difficult to believe that equilibrium could be attained under conditions of rapid cooling from the liquidus and attempted to show by references to the Bowen and Schairer (1935) phase diagram that the olivines contained too much magnesium relative to the pyroxenes. While this conclusion does not seem acceptable in terms of later experimental work (fig. 1), the degree to which equilibrium was approached and the temperatures

[1] Based on the Field Museum of Natural History collection.

represented by the observed meteorite distributions are far from clear. An interesting suggestion was made by Fredriksson (1963) that rapidly cooled chondrules would give rise to olivine grains of almost constant composition in a glassy matrix and that this matrix would later devitrify to pyroxene and plagioclase. Presumably, the glass would also have a nearly constant Mg and Fe^{2+} content. We have already discussed an extension of this idea in relation to Figure 4 in which the ideal limiting case of constant Mg/Fe^{2+} ratio for chondrules of varying olivine and pyroxene content was considered. We still need, however, to consider a mechanism by which the different chondrules can be derived.

It is possible to outline a scheme for obtaining the four major chondrule types through some unspecified process which brings about disruption of a liquid-crystal suspension so that separation of these components can occur. The general scheme is shown in Figure 8. Obviously, such a mechanism must be highly dependent on the ambient temperature and the kinetic properties of crystals and liquid. According to this scheme, the barred olivine and radiating enstatite chondrules come closest to representing possible liquids. Only the barred type would have a high probability of representing the liquid of the bulk meteorite composition, although it could also represent liquids of varying degrees of differentiation. In contrast, the radiating pyroxene type could, assuming it consists of almost pure pyroxene, represent only liquids near the pyroxene join.

The porphyritic condrules, at least where well developed, should indicate a period of relatively slow cooling and crystallization in the olivine field before the disruptive process. Consequently, their crystals should be more Mg-rich than those formed by quenching.

Presumably, the granular olivine chondrules are nearly pure olivine with most of the rest liquid excluded. They may in some cases be gradational into the porphyritic type.

An examination of thin sections shows that the various chondrules are frequently composites. Thus, for example, the composite porphyritic and barred olivine type observed in Allegan and the combined porphyritic and radiating types in Aussun may indicate a period of slow cooling before the ultimate quench. The porphyritic chondrules are usually not as abundant as other types so that any Mg-rich crystals they contain might go undetected.

If the unspecified disruptive process brings about a separation of crystals and liquid, the allowable variation is between the tie lines ol′-px′ and ol″-px″ of Figure 4 as already discussed. This allowable

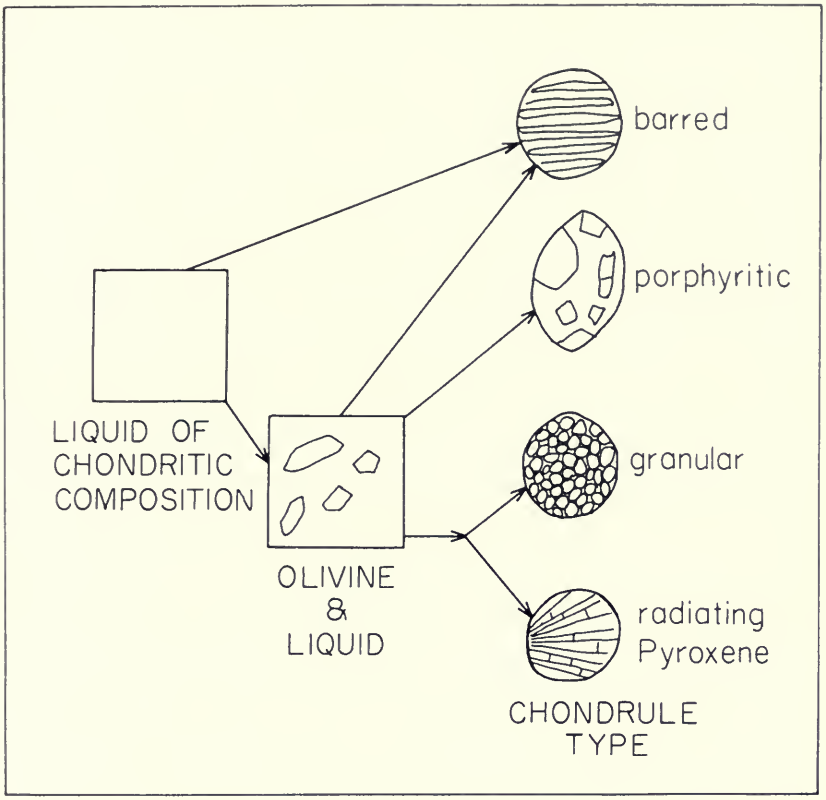

FIG. 8. General scheme for the derivation of various chondrule types by an unspecified, rapid disruptive process which brings about separation of crystals and liquid.

variation is not large and might be reduced by the chemical analytical limitations. However, we have already concluded that the ideal limiting case is probably not realized, so that we must either call upon a modified mechanism in which a distribution of Mg and Fe^{2+} occurs during quenching or one in which variations are annealed out below the liquidus. The nature of the distribution shown by Figure 1 indicates that if the former takes place, the distribution cannot have occurred between olivine and liquid or a liquid-like glass since the liquid is always richer in Fe^{2+} than either crystal. It may be that the extreme cases of Mg-rich olivine and Fe^{2+}-rich liquid are not realizable in a rapid quench but that a continuous rapid adjustment of olivine crystal to microcrystalline pyroxene or pyroxene-like glass represented by the tie lines is realizable. The only alternative to

this seems to be the annealing adjustment to an approximate equilibrium distribution between the olivine and devitrifying glass just below liquidus. The latter would be considered a form of metamorphism by some.

It seems likely that there is a close relation between the chondrule structures and the limitations imposed by crystallization kinetics. As an illustration, the widths of the bars in barred olivine chondrules are usually in the range of 10^{-2} mm. and this may represent the diffusion length of Si^{4+} at the temperature at which crystallization occurs. It would seem that such correlations would open a fruitful line of investigation in the future.

Chondrites of Variable Composition

These chondrites are characterized by a variability of composition of their olivines and pyroxenes both with respect to position within the specimen and by a lack of orderly distribution relations between the silicates. Significant variations of this type were found in eight chondrites by Keil and Fredriksson (1964). An extensive investigation of variability in the carbonaceous chondrite Murray was also made by Fredriksson and Keil (1964) and of Chainpur by Keil *et al.* (1964). Recently variation has also been found in 11 more chondrites by Dodd and Van Schmus (1965).

In the Chainpur chondrite (Keil *et al.*, 1964) both pyroxene and olivine from the same chondrule show values of $Fe^{2+}/(Fe^{2+}+Mg)$ of about 0.05 whereas in other chondrules the minerals are far more iron rich. Also, generally, the olivine shows a larger range of compositions than the associated pyroxene grains, which is compatible with a wider expected range of crystallization for the former mineral. In addition, some grains show marked compositional zoning with the iron content increasing outward. As was pointed out by Keil and Fredriksson (1964), this zonal structure and variability seems more compatible with a slower rate of cooling than one can imagine for the uniform chondrites.

In order to explain the coexistence of Mg-rich pyroxenes and olivines, we must call on a different mechanism. A suitable one is that of reduction of some of the meteoritic material which then becomes mixed with that which is more oxidized so that the average for the meteorite is attained. This is equivalent to moving the bulk composition point of the reduced material toward the Mg_2SiO_4-$MgSiO_3$ join, as has already been stated.

It seems that mixtures of materials of varying oxidation state is a characteristic also of many of the carbonaceous chondrites which as a class appear somewhat similar to the variable ordinary chondrites under discussion here. Dodd and Van Schmus (1965) interpreted the latter group as representing a recrystallization sequence based on correlation of such features as degree of variation of the iron content of olivines with the presence of glass and the extent of chondrule-matrix intergrowth. However, as these authors themselves pointed out, these correlations are very difficult and uncertain. In the opinion of the writers, even their interpretation of the Bruderheim chondrite as "strongly recrystallized" and as representing the end of the sequence is open to serious doubt. It is difficult, for example, to see how this meteorite could have retained its observed isotopic fractionation between chondrules and matrix if this were true (Merrihue, 1963). The observed properties of Bruderheim agree more closely with the scheme of rapid crystallization outlined here for the uniform chondrites.

CRITIQUE OF SOME PREVIOUS CONCLUSIONS ON THE CHONDRITES

Of the modern ideas on the origin of the chondrites and chondrules only those of Mason (1960) and Wood (1963a,b) rest primarily on a mineralogical base, so that they become valid subjects of this type of critique. Their authors have committed themselves to definite positions which are open to test by presently-available information.

Mason arrived at the opinion that chondrules were derived from pre-existing hydrous silicates by crystallization in the solid state, that they were analogous to porphyroblasts and resulted from thermal metamorphism. In view of the wealth of evidence presented here and elsewhere (Keil and Fredriksson, 1964) for a high temperature liquidus history, it would seem that this and analogous views are no longer tenable.

Wood argued that the ordinary chondrites were derived from parent material represented by the single specimen Renazzo by a type of "metamorphic" recrystallization. The Fe^{2+}-poor chondrules of this meteorite, which lie in a more oxidized matrix consisting of Fe^{2+}-rich ferrite and silicates (Mason and Wiik, 1962), were shown by him to be compatible with the oxidation state of a gas of solar composition at high temperatures ($\sim$2000°K). The matrix on the other hand presumably could be in equilibrium with the solar gas only at much lower temperatures, as is shown also by Figure 2. The mechanical mixture of these high and low temperature products

would, if heated, be expected to strive for an intermediate state. According to Wood (1963a), this was attained when "Fe^{2+} from the fine Fe_3O_4 grains diffused into the chondrule minerals." Wood (1963b) also presented a detailed set of time scales for this process operating at different temperatures. His calculations were presumably based on diffusion coefficients deduced by Naughton and Fujikawa (1959) (Wood, 1963a). Wood does not seem to have concerned himself with the necessity of exchanging Mg^{2+} ions in the same process, although this could in principle be the rate controlling factor. Also, the work of Naughton and Fujikawa refers to *intergranular* diffusion which, as is well known, is almost always much faster than lattice diffusion. Certainly the magnitude of the change required in Wood's hypothesis requires lattice diffusion to be the major type operative so that the time scales presented by him have no validity whatever.

The validity of Wood's scheme has also been challenged on other grounds. Keil and Fredriksson (1964) noted that contrary to his hypothesis there appeared to be no connection between the iron content of the silicates and the distinctness of chrondritic texture. Even a very cursory examination shows that some of the most iron-rich silicates occur in meteorites with well-defined chondrule structure, microlitic texture and glass. Wood himself (1963a, p. 169) notes features of several chondrites which are not possible to reconcile with his hypothesis, and says: ". . . in some respects the concept of thermal metamorphism taxes credibility." He concludes, nevertheless: "In spite of these difficulties, the evidence seems very strong to me that most of the ordinary chondrites have been metamorphosed."

In contrast to the contradictory character of Wood's scheme for chondrite metamorphism, his attempts to correlate the mineral chemistry with the physicochemical environment of the hypothetical solar nebula appears to form a valid approach. His application of the methods first introduced by Urey (1952) have the advantage of making use of stable mineral compounds rather than such substances as MgO, FeO, etc. However, we have seen that few meteorites are reduced enough to have been equilibrated with the solar gas at the high temperatures implied by their mineralogy. As Wood himself indicated, it is possible that condensation occurred in regions which had been relatively depleted in hydrogen so that more iron-rich silicates were possible. Perhaps this is a natural and predictable consequence of the processes which gave rise to the condensed bodies of our solar system.

ACKNOWLEDGMENTS

The writers would like to express their thanks to Dr. H. B. Wiik for making available to them several unpublished meteorite analyses, and to Mrs. Dorothy Walker for typing the manuscript. The writers are grateful to the National Science Foundation which provided support for this work under grants GP-3688 and GA-307.

TABLE 1.—Normalized mole fractions of bulk compositions, normative olivine (L) and ratios of oxidized to reduced iron (R) for 43 ordinary chondrites. The normalized mole fractions result from the subtraction from the original analyses of quantities of oxides corresponding to normative albite, anorthite, orthoclase, wollastonite, chromite, ilmenite and $Ca_3P_2O_8$. In the source column for the bulk analyses U & C refers to Urey and Craig (1953). Additional sources of analyses are as follows: Duke *et al.* (1961): Bruderheim; Mason (1963): Yonozu; Mason and Wiik (1961, 1963): Ottawa, Chateau Renard, Mocs, New Concord, Richardson, Estacado, and Knyahinya; Miyashiro (1962b,c): Kessen, Mino; Miyashiro *et al.* (1963a,b,c): Sone, Tomita, and Kasamatu; Murayama *et al.* (1962): Sasagase; Prior (1916b): Daniel's Kuil; Vilcsek (1959): Breitscheid; Wiik (1956, 1965): Farmington, Hamlet, Hokmark, Holbrook, Kyushu, Ochansk, Rose City, Tomhannock Creek, and Varvik. *Refers to chondrites for which mineral analyses exist (Keil and Fredriksson, 1964) and whose average values appear in the last two rows. These averages appear as points in Figure 3 with the corresponding tie lines. The values of L and R are plotted in Figure 5.

Name	Type	Source of Bulk Analysis	Bulk Mole Fraction MgO	FeO	SiO_2	L	R
Albareto*	L	U & C	0.4716	0.1625	0.3659	0.631	0.296
Allegan*	H	U & C	0.4848	0.1009	0.4143	0.231	0.186
Beaver Creek*	H	U & C	0.4677	0.1103	0.4219	0.248	0.206
Bjurböle	L	U & C	0.4798	0.1329	0.3873	0.476	0.243
Breitscheid*	H	Vilcsek	0.5154	0.0863	0.3984	0.318	0.154
Buderheim*	L	Duke *et al.*	0.4619	0.1421	0.3960	0.427	0.272
Chantonnay*	L	U & C	0.4790	0.1554	0.3656	0.595	0.285
Chateau Renard*	L	Mason & Wiik	0.4749	0.1289	0.3962	0.417	0.243
Collescipoli*	H	U & C	0.5348	0.0704	0.3948	0.308	0.125
Coon Butte*	L	U & C	0.4369	0.1406	0.4225	0.302	0.279
Daniel's Kuil	EC	Prior	0.4961	0.0001	0.5038	0	0
Djati-Pengilon*	H	U & C	0.4302	0.1566	0.4132	0.251	0.298
Ekeby*	H	U & C	0.4874	0.1249	0.3877	0.351	0.224
Estacado*	H	Mason & Wiik	0.4583	0.1354	0.4062	0.306	0.250
Farmington*	L	Wiik	0.4498	0.1496	0.4007	0.416	0.289
Forest City*	H	U & C	0.5013	0.0947	0.4040	0.286	0.169
Forksville	L	U & C	0.4515	0.1789	0.3696	0.577	0.321
Hamlet	L	Wiik	0.4462	0.1690	0.3848	0.554	0.357
Hessle*	H	U & C	0.4764	0.1250	0.3986	0.320	0.233
Hökmark*	L	Wiik	0.4449	0.1658	0.3893	0.361	0.239
Holbrook*	L	Wiik	0.4684	0.1218	0.4097	0.364	0.236
Homestead*	L	U & C	0.4698	0.1300	0.4002	0.376	0.242
Kasamatu	H	Miyashiro *et al.*	0.5048	0.0964	0.3988	0.303	0.175
Kesen*	H	Miyashiro	0.4916	0.1093	0.3991	0.292	0.197
Knyahinya*	L	Mason & Wiik	0.4498	0.1612	0.3889	0.521	0.341
Kyushu*	L	Wiik	0.4438	0.1520	0.4042	0.402	0.307
Merua*	H	U & C	0.4894	0.0832	0.4273	0.211	0.159
Mino	L	Miyashiro	0.4747	0.1352	0.3901	0.444	0.253
Mocs*	L	Mason & Wiik	0.4700	0.1194	0.4106	0.346	0.230
New Concord*	L	Mason & Wiik	0.4731	0.1203	0.4065	0.368	0.232

TABLE 1 (*Continued*)

Name	Type	Source of Bulk Analysis	Bulk Mole Fraction MgO	FeO	SiO_2	L	R
Oakley*	H	U & C	0.4857	0.1143	0.4000	0.326	0.212
Ochansk*	H	Wiik	0.5052	0.0835	0.4113	0.253	0.153
Ottawa	L	Mason & Wiik	0.4448	0.1763	0.3790	0.593	0.384
Richardton*	H	Mason & Wiik	0.4874	0.1173	0.3953	0.312	0.210
Rose City	H	Wiik	0.5136	0.0715	0.4148	0.191	0.132
Sasagase	H	Murayama *et al.*	0.4862	0.1073	0.4064	0.292	0.197
Soko-Banja*	L	U & C	0.4395	0.1681	0.3924	0.500	0.364
Sone	H	Miyashiro *et al.*	0.4891	0.1153	0.3956	0.329	0.210
Stalldalen*	H	U & C	0.4877	0.0935	0.4188	0.235	0.175
St. Michel	L	U & C	0.4776	0.1434	0.3790	0.504	0.263
Tomhannock Creek*	H	Wiik	0.4506	0.1559	0.3935	0.394	0.293
Tomita	L	Miyashiro *et al.*	0.4705	0.1333	0.3962	0.399	0.251
Varvik*	L	Wiik	0.4380	0.1765	0.3855	0.576	0.472
Yonozu	H	Mason	0.4878	0.1114	0.4008	0.304	0.204
Av H (Total)			0.4878	0.1075	0.4048	0.289	0.199
Av L (Total)			0.4598	0.1482	0.3919	0.462	0.290
Av H (K&F)			0.4846	0.1101	0.4053		
Av L (K&F)			0.4594	0.1454	0.3951		

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